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Aramid fibrils

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ARAMID FIBRILS

The present invention pertains to aramid fibrils, to a method of preparing said fibrils, and to paper made thereof.

Pulp is defined as fiber stem which is highly fibrillated. The fibrillated part is
5 mentioned fibrils, which are highly entangled and have a high aspect ratio (> 100)
and a large surface area ($8-10 \text{ m}^2/\text{g}$) which is about 40 times that of standard
filament. Thus aramid pulps are fibrillated particles that are used for making
paper, gaskets, breaking lines, and the like. Pulp generally can be made from
spun fiber, by performing cutting and fibrillation steps thereon. It is however
10 advantageous to directly made pulp, without first spinning the polymer to a fiber.
Such direct pulp making method has been disclosed in the art, for instance in
US 5,028,372. According to this method an aramid pulp was made by forming a
para-aramid polymer solution, extruding said solution, having an inherent
viscosity between 1 and 4, onto a conveyor, incubating the solution on the
15 conveyor until it forms a gel, and cutting this gel and isolating the pulp thereof.
The polymer has a concentration of 6 to 13 wt.% of the solution and the thus
obtained pulp has a specific surface area greater than $2 \text{ m}^2/\text{g}$.
It can be envisaged that for particular applications a highly fibrillated pulp is
advantageous. It would even be more advantageous that the polymeric material
20 is fully (or essentially fully) in the fibril form, i.e. does not longer contain fiber-like
material. In other word there is a need for "pulp" which only contains the fibrillated
part and no longer the fiber stems. Such material is unknown up to now. Very
useful properties could be expected from such materials, such as high flexibility,
high binding capacity in paper, and good porosity of papers made thereof.
25 Further, it can be expected that such material has a considerable hardness after
drying, and therefore suitable for using in composites. This material for the
purpose of this invention is defined as "fibrils".

The first objective of the present invention is therefore to provide an aramid polymer solution as a spinning dope, preferably exhibiting optical anisotropy, in order to obtain a spinning dope that can directly be spun without applying high pressure and/or high spinning temperature for making fibrils. Achievement of this
5 objective makes it possible to produce aramid fibrils of pre-determined length. These fibrils are not only curved, but further contain kinks, wherein in each kink the direction of the fibril changes sharply to form an angle.

It is therefore also an objective of the present invention to provide fibrils that
10 loses a large part of its fluffy character upon drying, but remain voluminous when wet. The fibrils according to this invention relates to a aramid fibrils having in the wet phase a Canadian Standard Freeness (CSF) value less than 300 ml and after drying a specific surface area (SSA) less than 7 m²/g.

15 The fibrils of this invention, which are not redispersable after drying, result in paper with very high paper strengths, and to very hard materials after drying.

Preferred fibrils according to the invention have in the wet phase the CSF value less than 150 ml and an SSA less than 1.5 m²/g.

20 The fibrils can be made from a meta and/or para-aramid polymer solution, such as poly(para-phenylene terephthalamide), poly(meta-phenylene isophthalamide), copoly(para-phenylene/3,4'-dioxydiphenylene terephthalamide) and the like, some of which polymers are commercially used in fibers and pulp available under the trade names Kevlar®, Twaron®, Conex®, and Technora®. The preferred
25 aramid is para-aramid, more preferably poly(para-phenylene terephthalamide).

Para-oriented aromatic polyamides are condensation polymers of a para-oriented aromatic diamine and a para-oriented aromatic dicarboxylic acid halide (hereinafter abbreviated to "para-aramids") and have hitherto been known to be
30 useful in various fields such as fiber, pulp and the like because of their high strength, high elastic modulus and high heat resistance.

As typical members of para-aramid are mentioned the aramids of which

structures have a poly-para-oriented form or a form close thereto, such as poly(paraphenylene terephthalamide), poly(4,4'-benzanilide terephthalamide), poly(paraphenylene-4,4'-biphenylenedicarboxylic acid amide) and poly (paraphenylene-2,6-naphthalenedicarboxylic acid amide). Among these para-
5 aramids, poly(paraphenylene terephthalamide) (hereinafter abbreviated to PPTA) is most representative.

Hitherto, PPTA has been produced in polar amide solvent/salt systems in the following manner. Thus, PPTA is produced by carrying out a solution
10 polymerization reaction in a polar amide solvent. The PPTA is precipitated, washed with water and dried, and once isolated as a polymer. Then, the polymer is dissolved in a solvent and made into a PPTA fiber by the process of wet spinning. In this step, concentrated sulfuric acid is used as the solvent of spinning dope, because PPTA is not readily soluble in organic solvents. This spinning
15 dope usually shows an optical anisotropy.

Industrially, PPTA fiber is produced from a spinning dope using concentrated sulfuric acid as a solvent, considering the performances as a long fiber, particularly strength and stiffness.

20

According to the closest prior art EP 381206 a process is disclosed for preparing subdenier fibers from lyotropic liquid crystalline polymer. The process comprises 1) extruding a stream of an optically anisotropic solution of a polymer into a chamber, 2) introducing a pressurized gas into said chamber, 3) directing the gas
25 in the flow direction of and in surrounding contact with said stream within the chamber, 4) passing both the gas and stream through an aperture into a zone of lower pressure at velocities sufficient to attenuate the stream and fragment it into fibers, and 5) contacting the fragmented stream in said zone with a trickle of coagulating fluid. The presently claimed process is adapted in order to prevent
30 the formation of subdenier fibers and to facilitate the formation of fibrils.

With the aim of rationalizing the prior process, there have also been proposed up to date various other processes for directly making a pulp from a liquid polymer

dope without separating the step of polymerization and the step of spinning from each other, among which the previously mentioned US 5,028,372, however none of these produce (fiber-free) fibrils.

- 5 In yet another objective of the present invention is to overcome the disadvantages of the common pulp-making processes, by providing a process for producing a stable polymer solution and a product of uniform quality according to an industrially advantageous and simplified method, and to obtain fibrils with a high relative viscosity. In order to obtain material with high relative viscosity in
10 one step, a polymer solution with low dynamic viscosity is required to easily form fibrils.

These and other objectives have been achieved by a process for making a polymer solution comprising the steps of:

- 15 a. polymerizing an aromatic diamine and an aromatic dicarboxylic acid halide to an aramid polymer, in a mixture of N-methylpyrrolidone or dimethylacetamide and calcium chloride or lithium chloride wherein at least part of the hydrochloric acid formed is neutralized, to obtain a neutralized dope having a polymer concentration of 2 to 6 wt.%,
20 b. converting the dope to fibrils by using a jet spin nozzle, and
c. coagulating the fibrils using a coagulation jet.

This method makes it possible to obtain an aramid polymer having a η_{rel} (relative viscosity) between 2.0 and 5.0.

25

According to a preferred embodiment of the invention a non-fibrous polymer solution of para-aramid in a mixture of NMP/CaCl₂, NMP/LiCl, or DMAc/LiCl has been made, wherein the polymer solution has a relative viscosity $\eta_{rel} > 2.2$.

- 30 The aramid polymer solution of the present invention exhibits a low dynamic viscosity at a temperature up to about 60° C in the shear rate range of 100 – 10,000 s⁻¹. For that reason the polymer solution according to the invention can be spun at a temperature below 60° C, preferably at room temperature. Further, the

aramid dope of the present invention is free from an extra component as pyridine and can be produced advantageously from the industrial point of view in that the production process can be simplified and the process is free from the problem of corrosion of apparatuses by concentrated sulfuric acid as compared with the prior
5 dopes using concentrated sulfuric acid as a solvent.

Further, according to the process of the present invention, the polymer solution can directly be spun, and the product can be made into fibrils, so that the process of production can be greatly simplified as compared with the prior
10 production processes of aramid pulp, which is usually made by first making the yarn.

An aramid paper having a long breaking length can be produced from the aramid fibrils of the present invention. When used as a starting material of friction
15 materials including paper for automatic transmission and the like, the performance is good. The fibrils are directly made from spinning the polymer solution, thus without making fibers.

The invention therefore also relates to aramid fibrils having a CSF (Canadian
20 Standard Freeness) of never dried fibrils of less than 300, preferably of less than 150. With more preference the para-aramid fibrils have a relative viscosity (η_{rel}) larger than 2.2.

In another embodiment the invention also pertains to aramid paper obtainable
25 from the fibrils of the invention. Such paper comprises at least 2 wt.%, preferably at least 5 wt.%, most preferably at least 10 wt.% of the aramid fibrils.

The present invention will now be explained in more detail below.

30 The stable spin dope has a para-aramid concentration of 2 - 6 wt.% and a moderate to high degree of polymerization to allow high relative viscosity (η_{rel} = about 2.0 to about 5.0). Depending on the polymer concentration the dope exhibits an anisotropic (polymer concentration = 2 to 6 wt.%) or an isotropic

behavior. Preferably, the dynamic viscosity η_{dyn} is smaller than 10 Pa.s, more preferably smaller than 5 Pa.s at a shear rate of 1000 s^{-1} . Neutralization takes place during or preferably after polymerizing the monomers forming the aramid. The neutralization agent is not present in the solution of monomers before
5 polymerization has commenced. Neutralization reduces dynamic viscosity by a factor of at least 3. The neutralized polymer solution can be used for direct fibrils spinning using a nozzle, contacting the polymer stream by pressurized air in a zone with lower pressure where the polymer stream is broken into droplets by expansion of the air. The droplets are attenuated into fibrils. Coagulation of the
10 fibrils takes place using a suitable coagulant as e.g. water or water/NMP/ CaCl_2 mixtures. Instead of CaCl_2 other chlorides such as LiCl may also be used. By adjusting the polymer flow / air flow ratio the length and the CSF of the fibrils can be changed. At high ratios long fibrils are obtained, while at low ratios short fibrils are obtained. The specific surface area (SSA) of the fibrils decreases with
15 decreasing Canadian Standard Freeness (CSF).
The fibrils of the present invention are useful as a starting material for para-aramid paper, friction materials including automobile brake, various gaskets, E-papers (for instance for electronic purposes, as it contains very low amounts of ions compared to para-aramid pulp made from sulfuric acid solutions), and the
20 like.

Examples of the para-oriented aromatic diamine usable in the present invention include para-phenylenediamine, 4,4'-diaminobiphenyl, 2-methyl-paraphenylenediamine, 2-chloro-paraphenylenediamine, 2,6-naphthalenediamine, 1,5-
25 naphthalenediamine, and 4,4'-diaminobenzanilide.

Examples of para-oriented aromatic dicarboxylic acid halide usable in the present invention include terephthaloyl chloride, 4,4'-benzoyl chloride, 2-chloroterephthaloyl chloride, 2,5-dichloroterephthaloyl chloride, 2-
30 methylterephthaloyl chloride, 2,6-naphthalenedicarboxylic acid chloride, and 1,5-naphthalenedicarboxylic acid chloride.

In the present invention 0.950-1.050 mole, preferably 0.980-1.030, more

preferably 0.995-1.010 mole of para-oriented aromatic diamine is used per 1 mole of para-oriented aromatic carboxylic acid halide in a polar amide solvent in which 0.5-4 wt.% of alkali metal chloride or alkaline earth metal chloride is dissolved (preferably 1-3 wt.%), making the concentration of para-aramid
5 obtained thereof 2-6 wt.%, preferably 2-4 wt.%, more preferably 2.5-3.5 wt.%. In the present invention the polymerization temperature of para-aramid is -20° C to 70° C, preferably 0° C to 30° C, and more preferably 5° C to 25° C. In this temperature range the dynamic viscosity is within the required range and the fibrils produced thereof by spinning can have sufficient degree of crystallization
10 and degree of crystal orientation.

An essential feature of the present invention is that the polymerization reaction may be first enhanced and thereafter stopped by neutralizing the polymer solution or the solution forming the polymer by adding an inorganic or strong organic
15 base, preferably calcium oxide or lithium oxide. In this respect the terms "calcium oxide" and "lithium oxide" comprise calcium hydroxide and lithium hydroxide, respectively. This neutralization effects the removal of hydrogen chloride, which is formed during the polymerization reaction. Neutralization results in a drop of the dynamic viscosity with a factor of at least 3 (with regard to non-neutralized
20 corresponding solution). Per mole of the amide group formed in the polycondensation reaction, after neutralization the chlorides are preferably present in an amount of 0.5-2.5 moles, more preferably in an amount of 0.7-1.4 moles. The total amount of chloride may originate from CaCl_2 , which is used in the solvent and from CaO , which is used as neutralizing agent (base). If the
25 calcium chloride content is too high or too low, the dynamic viscosity of the solution is raised too much to be suitable as a spin solution.

The liquid para-aramid polymerization solution can be supplied with the aid of a pressure vessel to a spinning pump to feed a nozzle of 100-1000 μm for air jet
30 spinning to fibrils. The liquid para-aramid solution is spun through a spinning nozzle into a zone of lower pressure. For air jet spinning more than 1 bar, preferably 4-6 bar is separately applied through a ring-shaped channel to the same zone where expansion of air occurs. Under the influence of the expanding

air flow the liquid spinning solution is divided into small droplets and at the same time or subsequently oriented by drawing. Then the fibrils are coagulated in the same zone by means of applying a coagulant jet and the formed fibrils are collected on a filter and washed. The coagulant is selected from water, mixtures of water, NMP and CaCl_2 , and any other suitable coagulant.

The present invention will now be explained by way of the following non-limitative examples.

- 10 The methods of test and evaluation and criteria of judgment employed in the examples and comparative examples were as follows.

Test methods

15 Relative viscosity

The sample was dissolved in sulfuric acid (96 %) at room temperature at a concentration of 0.25 % (m/v). The flow time of the sample solution in sulfuric acid was measured at 25° C in an Ubbelohde viscometer. Under identical conditions the flow time of the solvent is measured as well. The viscosity ratio is then calculated as the ratio between the two observed flow times.

Dynamic viscosity

The dynamic viscosity is measured using capillary rheometry at room temperature. By making use of the Powerlaw coefficient and the Rabinowitsch correction the real wall shear rate and the viscosity have been calculated.

Fiber length measurement

Fiber length measurement was done using the Pulp Expert™ FS (ex Metso). As length the average length (AL), the length weighted length (LL), weight weighted length (WL) is used. The subscript 0.25 means the respective value for particles with an average length ≥ 250 micron. The amount of fines was determined as the fraction of particles having a length weighted length (LL) < 250 micron.

This instrument needs to be calibrated with a sample with known fiber length. The calibration was performed with commercially available pulp as indicated in Table 1.

5 Table 1

Commercially available samples	AL mm	LL mm	WL mm	AL _{0.25} mm	LL _{0.25} mm	WL _{0.25} mm	Fines %
A	0.27	0.84	1.66	0.69	1.10	1.72	26.8
B	0.25	0.69	1.31	0.61	0.90	1.37	27.5
C	0.23	0.78	1.84	0.64	1.12	1.95	34.2

A Kevlar® 1F539, Type 979, Bale 102401587

B Twaron® 1095, Charge 315200, 24-01-2003

C Twaron® 1099, Ser.no.323518592, Art.no.108692

10 CSF

3 g (dry weight) of never dried fibrils are dispersed in 1 l water during 1000 beats in a Lorentz and Wettre desintegrator. A well-opened sample is obtained. The Canadian Standard Freeness (CSF) value is measured and corrected for slight differences in weight of the fibrils (Tappi 227).

15

Specific surface area (SSA) determination

Specific surface area (m²/g) was determined using adsorption of nitrogen by the BET specific surface area method, using a Gemini 2375 manufactured by Micromeretics. The wet fibrils samples were dried at 120° C overnight, followed by flushing with nitrogen for at least 1 h at 200° C.

20

Evaluation of optical anisotropy (liquid crystal state)

Optical anisotropy is examined under a polarization microscope (bright image) and/or seen as opalescence during stirring.

25

Paper strength

Hand sheets (70 g/m²) were made of 100 % fibril material or of 50 % fibril and 50 % Twaron® 6 mm fiber (Twaron® 1000). Tensile index (Nm/g) was measured according to ASTM D828 and Tappi T494 om-96 on dried paper (120° C), wherein sample width is 15 mm, sample length 100 mm, and test speed 10 mm/min at 21°C/65 % RH conditions.

30

Example 1

- Polymerization of para-phenyleneterephthalamide was carried out using a 2.5 m³ Drais reactor. After sufficiently drying the reactor, 1140 l of NMP/CaCl₂ (N-
- 5 methylpyrrolidone/ calcium chloride) with a CaCl₂ concentration of 2.5 wt.% were added to the reactor. Subsequently, 27.50 kg of para-phenylenediamine (PPD) were added and dissolved at room temperature. Thereafter the PPD solution was cooled to 10° C and 51.10 kg of terephthalic acid dichloride (TDC) were added. After addition of the TDC the polymerization reaction was continued for 45 min.
- 10 Then the polymer solution was neutralized with a calcium oxide/NMP-slurry (14.10 kg of CaO in 28 l NMP). After addition of the CaO-slurry the polymer solution was stirred for at least another 15 min. This neutralization was carried out to remove the hydrogen chloride (HCl), which is formed during polymerization. A gel-like polymer solution was obtained with a PPTA content of
- 15 4.5 wt.% and having a relative viscosity of 2.8 (in 0.25% H₂SO₄). The obtained solution exhibited optical anisotropy and was stable for more than one month. The solution was diluted with NMP until a polymer concentration of 3.0% was obtained.
- 20 The 3 % solution was supplied (120 l/h) to a spinning pump to feed a spinning nozzle with 20 holes of 350 µm. The spinning temperature was ambient. The PPTA was spun through the nozzle into a zone of lower pressure. An air jet of 6 bar (160 Nm³/h) (normal cube per hour) was separately applied perpendicularly to the polymer stream through ring-shaped channels to the same zone where
- 25 expansion of the air occurred. Thereafter, the fibrils were coagulated (H₂O/30 % NMP/1.3 % CaCl₂) in the same zone by means of applying a coagulant jet (600 l/h) through ring-shaped channels under an angle in the direction of the polymer stream and the formed fibrils were collected on a filter and washed.
- The spun fibrils have a CSF value of 83 ml characteristic for fibrils, while they
- 30 have a SSA of only 0.63 m²/g. When looking under a microscope a very fine structure is seen, which confirms the low CSF value.

Example 2

Polymerization of para-phenyleneterephthalamide was carried out using a 160 l Drais reactor. After sufficiently drying the reactor, 64 l of NMP/CaCl₂ (N-methylpyrrolidone/ calcium chloride) with a CaCl₂ concentration of 2.5 wt.% were added to the reactor. Subsequently, 1487 g of para-phenylenediamine (PPD) were added and dissolved at room temperature. Thereafter the PPD solution was cooled to 10° C and 2772 g of TDC were added. After addition of the TDC the polymerization reaction was continued for 45 min. Then the polymer solution was neutralized with a calcium oxide/NMP-slurry (776 g of CaO in NMP). After addition of the CaO-slurry the polymer solution was stirred for at least another 15 min. This neutralization was carried out to remove the hydrogen chloride (HCl), which is formed during polymerization. A gel-like polymer solution was obtained with a PPTA content of 4.5 wt.% and having a relative viscosity of 2.7 (in 0.25 % H₂SO₄). The obtained solution exhibited optical anisotropy and was stable for more than one month. The solution was diluted with NMP until a polymer concentration of 3.6 % was obtained.

The 3.6 % PPTA solution was supplied (16 kg/h) to a spinning pump to feed a spinning nozzle with 4 holes of 350 µm. The spinning temperature was ambient. The PPTA was spun through the nozzle into a zone of lower pressure. An air jet of 7 bar (45 Nm³/h) was separately applied perpendicularly to the polymer stream through ring-shaped channels to the same zone where expansion of the air occurred. Thereafter, the fibrils were coagulated in the same zone by means of applying a water jet (225 l/h) through ring-shaped channels under an angle in the direction of the polymer stream and the formed fibrils were collected on a filter and washed.

The collected fibrils show higher SSA values, but still the SSA decreases while the CSF value also decreases (see Table 2).

Table 2

CSF	SSA
(ml)	(m ² /g)
85.00	4.96
70.00	4.33
55.00	3.80

Example 3

- 5 Paper was made of the fibrils of Example 1. The paper strength of 50 % Twaron® 1000 6 mm fiber and 50 % fibrils was 23 Nm/g.

Example 4

- 10 Paper was made of the fibrils of Example 2. The paper strength of 50 % Twaron® 1000 6 mm fiber and 50 % fibrils was 18 Nm/g. The paper strength of paper consisting of 100 % fibrils was 10.8 Nm/g.

Claims:

- 5 1. Aramid fibrils having in the wet phase a Canadian Standard Freeness (CSF) value less than 300 ml and after drying a specific surface area (SSA) less than 7 m²/g.
2. The fibrils of claim 1 wherein in the wet phase the CSF value is less than 150 ml and after drying the SSA is less than 1.5 m²/g.
- 10 3. The fibrils of any one of claims 1-2 wherein the aramid is para-aramid, preferably poly(para-phenylene terephthalamide).
4. A method of preparing the fibrils of claims 1-3 comprising the steps
 - 15 a. polymerizing an aromatic diamine and an aromatic dicarboxylic acid halide to an aramid polymer, in a mixture of N-methylpyrrolidone or dimethylacetamide and calcium chloride or lithium chloride wherein at least part of the hydrochloric acid formed is neutralized, to obtain a neutralized dope having a polymer concentration of 2 to 6 wt.%,
 - b. converting the dope to fibrils by using a jet spin nozzle, and
 - c. coagulating the fibrils using a coagulation jet.
- 20 5. The method according to claim 4 wherein the η_{rel} (relative viscosity) of the aramid polymer is between 2.0 and 5.0.
6. A paper made of constituents comprising at least 2 wt.%, preferably at least 5 wt.%, most preferably at least 10 wt.% of the aramid fibrils of any one of claims 1-3.

Abstract:

The invention relates to aramid fibrils having in the wet phase a Canadian Standard Freeness (CSF) value less than 100 ml and after drying a specific surface area (SSA) less than $7 \text{ m}^2/\text{g}$, and to a method of preparing the fibrils of claims 1-5 comprising the steps

- 5 a. polymerizing an aromatic diamine and an aromatic dicarboxylic acid halide to an aramid polymer, in a mixture of N-methylpyrrolidone or dimethylacetamide and calcium chloride or lithium chloride wherein at least part of the hydrochloric acid formed is neutralized, to obtain a neutralized dope having a polymer concentration of 2 to 6 wt.%,
- 10 b. converting the dope to fibrils by using a jet spin nozzle, and
- c. coagulating the fibrils using a coagulation jet.

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